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UTILITY PATENT APPLICATION TRANSMITTAL

(Only for new nonprovisional applications under 37 CFR 1.53(b))

Attorney Docket No. 3028.1US (96-0761.1)

First Inventor or Application Identifier Whonchee Lee

Title HIGH SELECTIVITY BPSG TO TEOS ETCHANT

Express Mail Label No. EL312581941US

APPLICATION ELEMENTS

See MPEP chapter 600 concerning utility patent application contents.

1. ☒ * Fee Transmittal Form (e.g., PTO/SB/17)
(Submit an original, and a duplicate for fee processing)
2. ☒ Specification [Total Pages 7]
(preferred arrangement set forth below)
 - Descriptive title of the invention
 - Cross References to Related Applications
 - Statement Regarding Fed sponsored R & D
 - Reference to Microfiche Appendix
 - Background of the invention
 - Brief Summary of the invention
 - Brief Description of the Drawings (if filed)
 - Detailed Description
 - Claim(s)
 - Abstract of the Disclosure
3. ☒ Drawing(s) (35 U.S.C. 113) [Total Sheets 3]
4. Oath or Declaration [Total Pages 2]
 - a. ☐ Newly executed (original or copy)
 - b. ☒ Copy from a prior application (37 C.F.R. § 1.63(d))
(for continuation/divisional with Box 17 completed)
[Note Box 5 below]
 - i. ☐ DELETION OF INVENTOR(S)
Signed statement attached deleting inventor(s) named in the prior application, see 37 C.F.R. §§ 1.63(d)(2) and 1.33(b).
5. ☒ Incorporation By Reference (useable if Box 4b is checked)
The entire disclosure of the prior application, from which a copy of the oath or declaration is supplied under Box 4b, is considered to be part of the disclosure of the accompanying application and is hereby incorporated by reference therein.

ADDRESS TO:

Assistant Commissioner for Patents
Box Patent Application
Washington, DC 20231

6. ☐ Microfiche Computer Program (Appendix)
7. Nucleotide and/or Amino Acid Sequence Submission (if applicable, all necessary)
 - a. ☐ Computer Readable Copy
 - b. ☐ Paper Copy (identical to computer copy)
 - c. ☐ Statement verifying identity of above copies

ACCOMPANYING APPLICATION PARTS

8. ☐ Assignment Papers (cover sheet & document(s))
9. ☐ 37 C.F.R. § 3.73(b) Statement ☐ Power of Attorney
(when there is an assignee)
10. ☐ English Translation Document (if applicable)
11. ☒ Information Disclosure Statement (IDS)/PTO-1449 ☐ Copies of IDS Citations
12. ☐ Preliminary Amendment
13. ☒ Return Receipt Postcard (MPEP 503)
(Should be specifically itemized)
14. ☐ * Small Entity Statement(s) ☐ Statement filed in prior application, Status still proper and desired (PTO/SB/09-12)
15. ☐ Certified Copy of Priority Document(s)
(if foreign priority is claimed)
16. ☐ Other:

* A new statement is required to be entitled to pay small entity fees, except where one has been filed in a prior application and is being relied upon.

17. If a CONTINUING APPLICATION, check appropriate box, and supply the requisite information below and in a preliminary amendment:

☐ Continuation ☒ Divisional ☐ Continuation-in-part (CIP) of prior application No: 09 / 056,323

Prior application information: Examiner V. Perez Ramos

Group / Art Unit: 1765

18. CORRESPONDENCE ADDRESS

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Signature	[Signature]		Date
			07/22/1999

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PATENT
Attorney Docket 3028.1US (96-0761.1)

NOTICE OF EXPRESS MAILING

Express Mail Mailing Label Number: EL312581941US

Date of Deposit with USPS: July 22, 1999

Person making Deposit: Jared S. Turner

APPLICATION FOR LETTERS PATENT

for

HIGH SELECTIVITY BPSG TO TEOS ETCHANT

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HIGH SELECTIVITY BPSG TO TEOS ETCHANT

BACKGROUND OF THE INVENTION

5 Cross Reference to Related Application: This application is a divisional of application Serial No. 09/056,323, filed April 7, 1998, pending.

10 Field of the Invention: The present invention relates to etchant formulations for semiconductor device production. More particularly, the present invention relates to an etchant formulation with high selectivity between BPSG and TEOS and methods for use of the formulation.

15 State of the Art: Etching is a process for removing material in a specific area through a wet (liquid) or dry (gaseous/vapor) chemical reaction, or by physical removal (such as by sputter etch, in which the specific area is bombarded with radio frequency-excited ions to knock atoms from the specific area). Etching is used in a variety of applications in the fabrication of semiconductor devices. For illustration purposes, vapor etching of bit line openings for a DRAM (Dynamic Random Access Memory) will be discussed.

20 A widely-utilized DRAM manufacturing process utilizes CMOS (Complimentary Metal Oxide Semiconductor) technology to produce DRAM circuits which circuits, comprise an array of unit memory cells, each typically including one capacitor and one transistor, such as a field effect transistor ("FET"). In the most common circuit designs, one side of the transistor is connected to one side of the capacitor, the other side of the transistor and the transistor gate are connected to external circuit lines called the bit line and the word line, and the other side of the capacitor is connected to a reference voltage that is typically one-half the internal circuit voltage. In such memory cells, an electrical signal charge is stored in a storage node of the capacitor connected to the transistor which charges and discharges the circuit lines of the capacitor.

25 It is known that hydrofluoric acid can be used as an etchant and is selective for BPSG to TEOS. In fact, the selectivity for BPSG to TEOS with hydrofluoric acid alone can be as high as 1000:1 in vapor etch and as low as less than 10:1 for dilute hydrofluoric
30

acid solutions. However, there are some disadvantages associated with vapor etch such as high particle counts and low productivity. Consequently, a wet etchant which could perform the role of high selective vapor would be advantageous.

Therefore, it would be desirable to develop an etchant and a method of use which would eliminate the risk of damaging the surface of the semiconductor substrate without having to use an etch stop layer.

SUMMARY OF THE INVENTION

The present invention relates to an organic acid/fluoride-containing solution etchant formulation having high selectivity for BPSG to TEOS and methods for its use in the production of semiconductor devices.

It has been found that the addition of an organic acid (such as acetic acid, formic acid, and oxalic acid) to a fluoride-containing solution (such as hydrofluoric acid and ammonium fluoride) dramatically increases selectivity of BPSG to TEOS without the above-mentioned disadvantages. As mentioned above, most applications with both BPSG and TEOS layers involve using the TEOS layer to prevent contamination of other components in a semiconductor device by the boron and phosphorous in the BPSG. Thus, a typical application consists of a layer of TEOS deposited over the semiconductor device components which require protection and a layer of BPSG applied over the TEOS layer. The etchant of the present invention may be used to etch desired areas in the BPSG layer. The high selectivity for BPSG to TEOS of etchant of the present invention would result in the TEOS layer acting as an etch stop. A second etch may be utilized to etch the TEOS layer. The etchant for the second etch can be less aggressive and, thus, not damage the components underlying the TEOS layer.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

While the specification concludes with claims particularly pointing out and distinctly claiming that which is regarded as the present invention, the advantages of this

invention can be more readily ascertained from the following description of the invention when read in conjunction with the accompanying drawings in which:

FIGs. 1-5 are side cross-sectional views of a method of forming an opening using an etchant according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

As previously discussed, hydrofluoric acid is a known etchant for etching BPSG and TEOS. However, it has been found that the addition of an organic acid (such as acetic acid, formic acid, and oxalic acid) to a fluoride-containing solution (such as hydrofluoric acid and ammonium fluoride (preferably 40% NH_4F in water)) dramatically increases selectivity of BPSG to TEOS. Most preferably, the etchant comprises an acetic acid/hydrofluoric acid mixture.

Etchants were formulated from glacial acetic acid (99.7% by weight in water) and hydrofluoric acid (49% by weight in water). The results (etch rate, selectivity and uniformity) of various etchant formulations are presented in Table 1, as follows:

TABLE 1

Etchant (vol. ratio glacial acetic acid to 49% HF)	Etching rate through TEOS ($\text{\AA}/\text{min}$)	Etching rate through BPSG ($\text{\AA}/\text{min}$)	BPSG Standard Deviation (%)	Selective ratio (BPSG/TEOS)
200:1	2.2	59	0	27
100:1	4.6	193	2.4	42
50:1	11.6	638	13.7	55

As it can be seen from Table 1, the selectivity and uniformity increased with increasing hydrofluoric acid concentration. The preferred etchant to obtain high selectivity and good uniformity is 100:1 volume ratio of 99.7% glacial acetic acid to 49%

hydrofluoric acid. However, it is believed that etchant ratios ranging from 1:1 to 500:1 will achieve adequate selectivity.

FIGs. 1-5 illustrate a technique for utilizing an etchant of the present invention in the formation of an opening in a BPSG layer. FIG. 1 illustrates an intermediate structure 100 comprising a substrate 102 having a first side 104 with a first barrier layer 106 of TEOS applied thereover. A second barrier layer 108 of BPSG is deposited over the first TEOS barrier layer 106.

A nitride layer 110 is patterned over the second barrier layer 108 of BPSG and has at least one opening 112, as shown in FIG. 2. The second barrier layer 108 of BPSG is etched with an etchant of the present invention to form a partial opening 114. Since the etchant of the present invention is selective to BPSG, the etch effectively ceases at the first barrier layer 106 of TEOS, as shown in FIG. 3. The first barrier layer 106 of TEOS is then etched with a less aggressive etchant, such as a TMAH / hydrofluoric acid mixture or a 35-40% by weight ammonium fluoride / 4-6% by weight phosphoric acid solution in water, which is less damaging to the substrate 102, to form a full opening 120, as shown in FIG. 4. The nitride layer 110 is stripped, as shown in FIG. 5.

It is, of course, understood that the etchant of the present invention can be utilized in any etching situation where selectivity of BPSG to TEOS barrier layers is desired, such as contact openings, container etching, and the like. Furthermore, the etchant of the present invention can be utilized in processes, such as a double side container process, wherein no masking step is required.

* * * * *

Having thus described in detail preferred embodiments of the present invention, it is to be understood that the invention defined by the appended claims is not to be limited by particular details set forth in the above description as many apparent variations thereof are possible without departing from the spirit or scope thereof.

CLAIMS

What is claimed is:

1. An etchant solution which is selective of borophosphosilicate glass to tetraethyl orthosilicate, said etchant solution comprising an organic acid and a fluoride-containing solution.
2. The etchant of claim 1, wherein said organic acid is selected from the group consisting of acetic acid, formic acid, and oxalic acid.
3. The etchant of claim 1, wherein said fluoride-containing solution is selected from the group consisting of hydrofluoric acid and ammonium fluoride.
4. The etchant of claim 1, wherein said organic acid comprises 99.7% acetic acid by weight in water and said fluoride-containing solution comprises 49% hydrofluoric acid by weight in water.
5. The etchant of claim 4, wherein said acetic acid is in a volumetric ratio with said hydrofluoric acid from between about 1:1 to 500:1.
6. The etchant of claim 5, wherein said acetic acid is in a volumetric ratio with said hydrofluoric acid at about 10:1 to about 100:1.
7. The etchant of claim 1, wherein said organic acid comprises 99.7% acetic acid by weight in water and said fluoride-containing solution comprises 40% ammonium fluoride acid by weight in water.
8. The etchant of claim 1, wherein said etchant solution includes a selectivity ratio of borophosphosilicate glass to tetraethyl orthosilicate between about 27:1 and 55:1.

ABSTRACT OF THE DISCLOSURE

An organic acid/fluoride-containing solution etchant having high selectivity for BPSG to TEOS. In an exemplary situation, a TEOS layer may be used to prevent contamination of other components in a semiconductor device by the boron and phosphorous in a layer of BPSG deposited over the TEOS layer. The etchant of the present invention may be used to etch desired areas in the BPSG layer, wherein the high selectivity for BPSG to TEOS of etchant would result in the TEOS layer acting as an etch stop. A second etch with a known etchant may be utilized to etch the TEOS layer. The known etchant for the second etch can be less aggressive and, thus, not damage the components underlying the TEOS layer.

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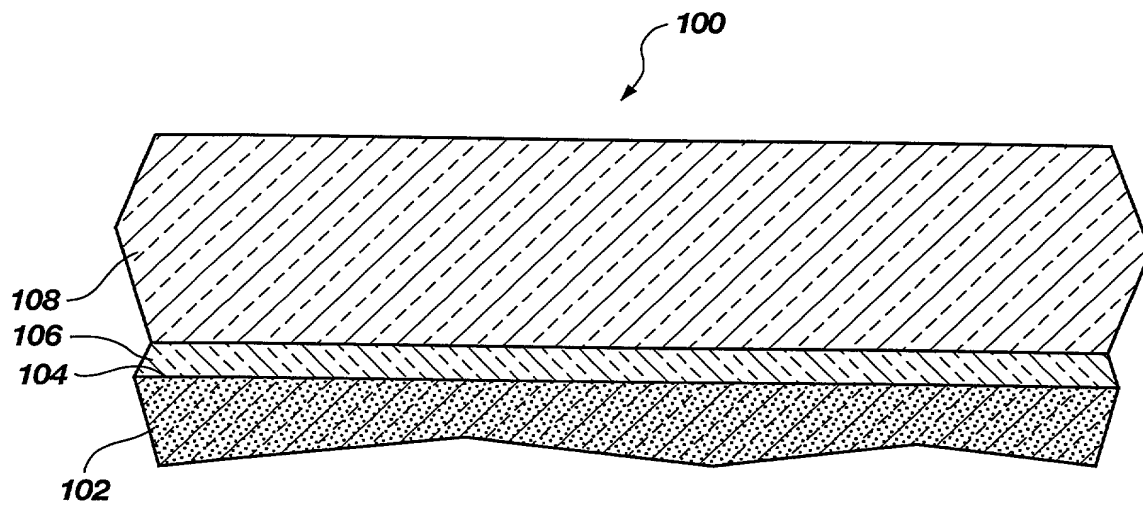


Fig. 1

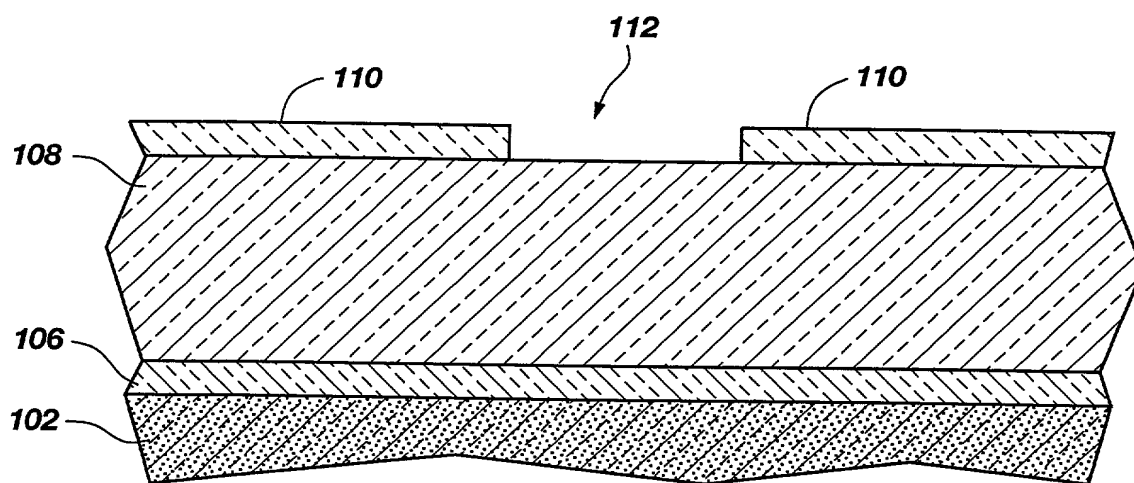


Fig. 2

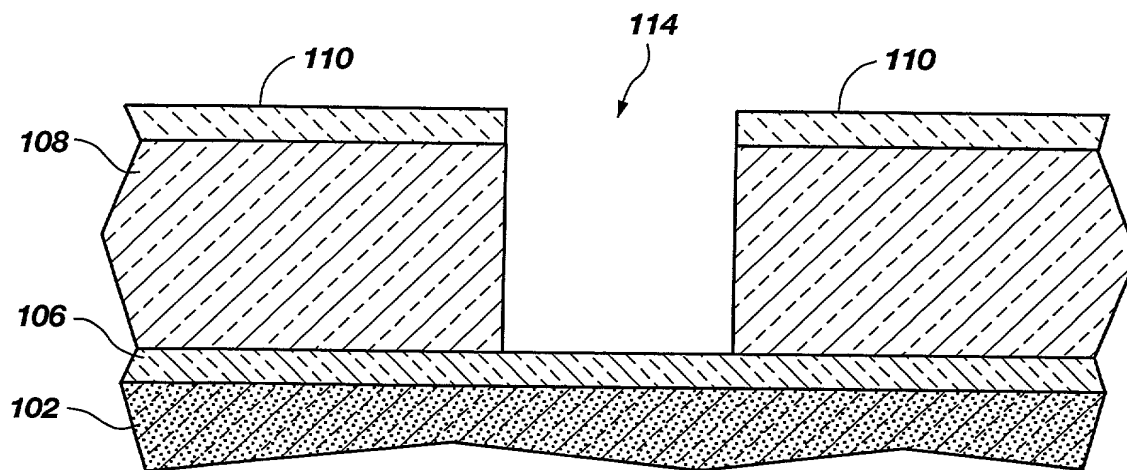


Fig. 3

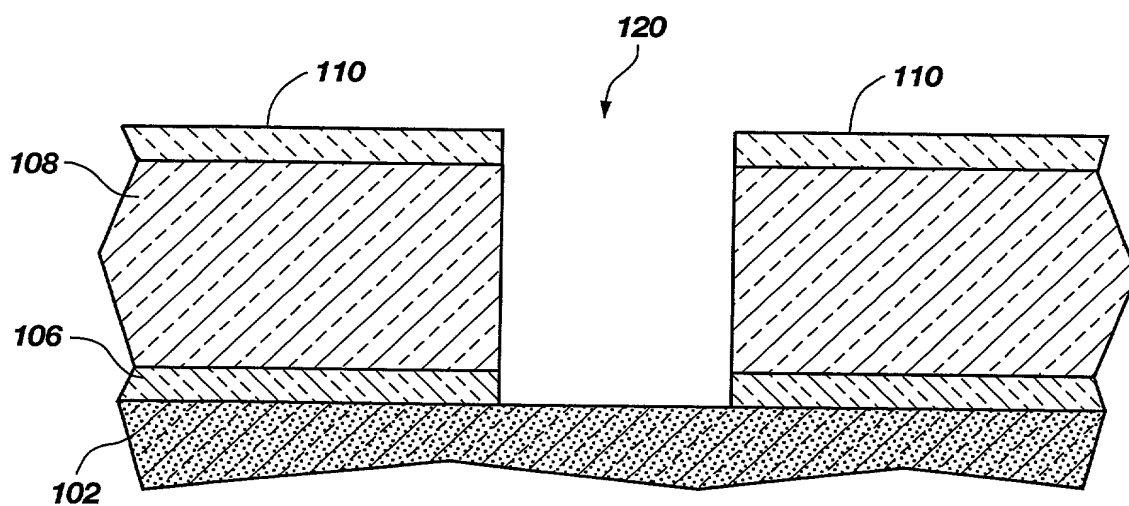


Fig. 4

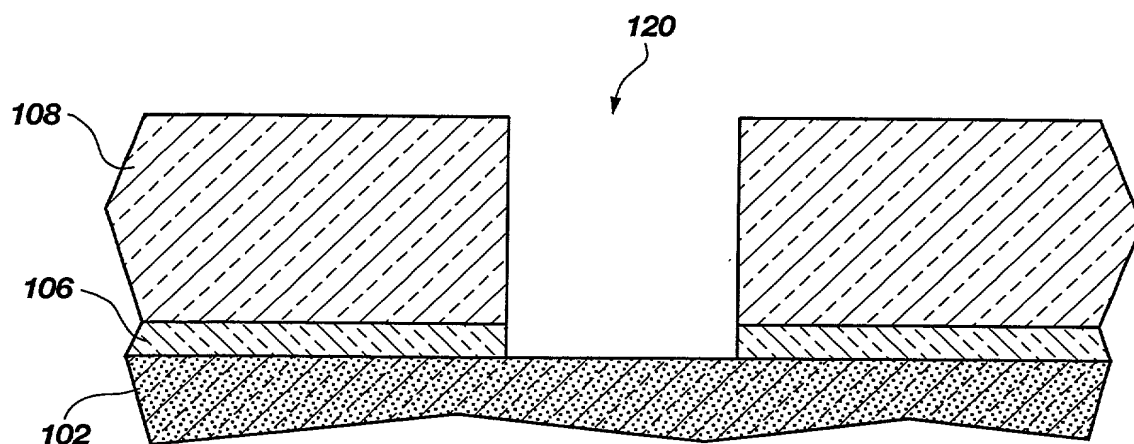


Fig. 5

DECLARATION FOR PATENT APPLICATION (WITH POWER OF ATTORNEY)

As an inventor named below or on any attached continuation page, I hereby declare that:

My residence, post office address and citizenship are as stated next to my name.

I believe that I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled HIGH SELECTIVITY BPSG TO TEOS ETCHANT, the specification of which (check one):

☒ is attached hereto.

☐ was filed on _____ as United States application serial no. _____ and was amended on _____.

☐ was filed on _____ as PCT international application no. _____ and was amended under PCT Article 19 on _____.

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the U.S. Patent and Trademark Office all information known to me to be material to the patentability of the subject matter claimed in this application, as "materiality" is defined in Title 37, Code of Federal Regulations § 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, § 119 (a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate or § 365(a) of any PCT international application(s) designating at least one country other than the United States of America listed below and on any attached continuation page and have also identified below and on any attached continuation page any foreign application for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America having a filing date before that of the application(s) on which priority is claimed.

Prior foreign/PCT application(s):

			Priority Claimed	
(number)	(country)	(day/month/year filed)	Yes	No
_____	_____	_____	_____	_____
(number)	(country)	(day/month/year filed)	Yes	No

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s) or § 365(c) of PCT international application(s) designating the United States of America listed below and on any attached continuation page and, insofar as the subject matter of each of the claims of this application is not disclosed in any such prior application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose to the U.S. Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations § 1.56 which became available between the filing date of such prior application and the national or PCT international filing date of this application:

(application serial no.)	(filing date)	(status - pending, patented or abandoned)
_____	_____	_____
(application serial no.)	(filing date)	(status - pending, patented or abandoned)
_____	_____	_____

I hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below:

(provisional application no.)	(filing date)
_____	_____
(provisional application no.)	(filing date)
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(provisional application no.)	(filing date)
_____	_____

I hereby appoint the following Registered Practitioners to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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 Citizenship: Taiwan, R.O.C.
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Date

3/21/98

DECLARATION FOR PATENT APPLICATION
(continuation page)

Invention title: HIGH SELECTIVITY BPSG TO TEOS ETCHANT

Inventor name(s) appearing on first declaration page: Whonchee Lee

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